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Effect of coagulation time, number of coagulation bath and ingredients on properties of continuous graphene oxide fibre

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The effect of coagulation time, the number of coagulation bath and ingredients on the properties of continuous graphene oxide fibre has been analyzed. It is observed that the number of coagulation baths and coagulation time affect the fibre morphology, electrical conductivity, and tenacity of fibre. Also, addition of the ingredient (ethylenediamine) results in lower strength and highest fibre count together with darker, curly, and rough fibre structure. It can be suggested that among all the samples, the sample with 1 coagulation bath and 2 min coagulation time can be preferred if electrical conductivity is more important than fibre tenacity. However, if fibre tenacity is the issue, preference of the sample with 3 coagulation baths and 2 min coagulation time will be more convenient.

Keywords: Coagulation time, Electrical conductivity, Ethylenediamine, Fibre morphology Graphene oxide fibre, Number of coagulation bath, Tenacity

1 Introduction

Graphene is a single sheet of graphite or a layer of carbon atoms in a two-dimensional honeycomb lattice structure¹. Since last decade, there has been growing interest on graphene and graphene-based materials due to their elevated high specific surface area, strength, high thermal and electrical conductivity; which give rise to its use in many fields such as conductive electrodes, photodetectors, batteries, electronic textile based on fibre etc. However, graphene has poor dispersion that makes it difficult to use for wet-spun or melt-spun polymer composite production. Thus, graphene derivatives such as graphene oxide are currently used in fibre production²⁻⁴. Graphene oxide (GO) is one of the most-used forms of graphene, which is obtained by adding functional groups on graphene. Graphene oxide has attracted enormous attention of current researches in terms of large-scale production due to its cost effectiveness, better dispersibility and mechanical properties, ease of processing and high unidirectional properties^{2,3}. The most significant application of graphene oxide is its reduction into graphene structures. After reduction, graphene structure is formed, which can be used in engineering applications, sensors, drug delivery systems, photovoltaic devices, etc⁵.

As known, graphene derived from graphene oxide can be used in many different forms such as fibres, hybrid fibres, thin films and composites with various polymers. For practical applications, production of continuous graphene fibres from graphene oxide liquid crystals is of major importance, since 2004 when Novoselov *et al.*⁶ were able to obtain single layer graphite structures. Wet spinning is the effective method for continuous graphene oxide fibre or graphene fibre production. Studies on continuous graphene oxide (GO) or graphene fibre production by wet spinning started since 2011 (ref. 7). In the wet spinning technique, the graphene oxide is treated in a coagulation bath followed by the reduction process to obtain graphene fibre. Ethanol, methanol, sodium hydroxide, acetone, cetyl trimethyl ammonium bromide (CTAB), etc. are the main ingredients of the coagulation baths^{2,8-10}. Selection of the chemicals and their concentration affect the fibre properties such as size, flexibility, conductivity, and mechanical properties¹¹. Graphene oxide (GO) itself has low electrical conductivity, so an additional reduction step after wet spinning is required to make the resultant fibres with more electrical conductivity⁵.

Xu and Gao⁸ obtained GO fibres by wet spinning of GO liquid crystals (GO LCs) by coagulation in a NaOH/methanol bath⁸. In another study, Xu and Gao⁹ obtained various graphene derivatives by free radical polymerization, chemical grafting, and nanoparticle

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decoration, and then compared the liquid crystal behavior of these various derivatives. The grafted derivatives were found to have better dispersion compared to other forms of graphene. They found that the use of coagulation baths containing different ions enhances the mechanical properties of the resultant fibres. Chen *et al.*² studied the properties of GO fibres, which are produced from small and large area GO sheets by wet spinning method. Graphite flakes were subjected to chemical oxidation to form GO sheets. Afterwards, GO sheets were injected through coagulation bath consisting of 5% wt NaOH. It was found that the fibre diameters are related to capillary diameters which also affect the orientation of the graphene sheets. In addition, increased orientation along the fibres improved the mechanical properties of the graphene oxide fibres. Aboutalebi *et al.*¹⁰ also produced GO fibres and yarns from graphene oxide liquid crystals by using an acetone coagulation bath and wet spinning technique. Heat treatment was preferred for reduction to minimize restacking and maintaining the surface area as well as the minimum required functional groups during the reduction step. Jalili *et al.*¹¹ produced graphene fibre from GO liquid crystals using a single step wet spinning process and analyzed the thermal conductivity and mechanical properties of GO fibres and reduced GO fibres. Huang *et al.*¹² used wet spinning method to obtain elastic graphene fibres from graphene oxide hydrogel. By changing the spinning parameters, graphene fibres and graphene ribbons were manufactured. The graphene ribbons were found to be highly elastic with high elastic recovery and improved electrical properties, which can be a candidate for flexible/wearable sensor applications. Xiang *et al.*¹³ obtained GO fibres by stable wet spinning process from high concentrated GO solutions (7%). Large and small GO flakes from single step oxidation were used and increased specific stress, modulus, and elongation were observed on the large flake GO fibres. Sun *et al.*¹⁴ fabricated graphene ribbons by applying shear stress during wet spinning of GO sheets prepared by modified Hummer's method. The ribbon formation was predicted to be due to the electrostatic interaction and chitosan coagulation bath. Other than fibres having only graphene derivatives, composite fibres have also been studied. In addition, hollow fibres are also interested to increase the surface area of graphene based fibres.

Huang *et al.*¹⁵ used a coagulation bath consisting of the CaCl_2 /ethanol solution to obtain wet-spun GO

fibres followed by a chemical reduction with either hydrazine (N_2H_4) or hydroiodic acid (HI). Fibres formed with different chemical reductions were compared in terms of cross-section, electrochemical properties, etc. Due to higher capacitance, HI reduced fibres were found to be better for use in supercapacitors.

As seen above from the literature, there is a limited number of studies on continuous graphene oxide fibre by wet spinning. These limited studies were mostly focused on the change of ingredients in the coagulation baths or application of different reduction type on GO fibre or dimension of GO sheets or nozzle type or composite GO fibre. Therefore, in this work, the effect of the number of coagulation baths and coagulation time on the formation of graphene oxide fibres has been studied and their mechanical, electrical and morphological properties are analyzed by SEM, FTIR, tensile tester and electrical conductivity meter device. Three different number of coagulation baths, such as 5, 3 and 1 baths and three different coagulation times, such as 10, 5 and 2 min, have been studied. In one study, the effect of the ingredient in the coagulation bath, i.e. ethylenediamine, on the properties of GO fibre has also been examined.

2 Materials and Methods

2.1 Materials

Graphene-iGP (diameter 44 μm , thickness 50-100 nm) was purchased from Grafen Chemical Industries, Ltd. Potassium permanganate (KMnO_4), sulfuric acid (H_2SO_4), hydrochloric acid (HCl), ethanol ($\text{C}_2\text{H}_5\text{OH}$), ethylenediamine ($\text{C}_2\text{H}_8\text{N}_2$) and calcium chloride (CaCl_2) were purchased from Merck, Ltd. Sodium nitrate (NaNO_3) and hydrogen peroxide 30 % (H_2O_2) were used for the study.

2.2 Methods

2.2.1 Production of Graphene Oxide Dispersion

Graphene oxide suspension was produced according to Hummer's method¹⁶. The solution was then washed with 1 M HCl solution 3 times at 5500 rpm in the centrifuge (Nuve, NF800R) to remove the impurities. For the pH adjustment, the solution was washed many times with distilled water until the solution pH is reached at 5-6. Further, this solution was dispersed by the mechanical homogenizer (WiseTis Homogenizer, HG-15D) to prepare the GO dispersion for the production of GO fibres by wet spinning method.

2.2.2 Production of Graphene Oxide Fibres by Wet Spinning

The wet spinning method was performed with a laboratory type syringe pump (Longfian Scitech, JAZ-C6) at a feeding rate of 10ml/h and the viscous GO dispersion obtained was injected into coagulation baths with different ingredients. The GO dispersion was immersed into the ethanol/distilled water (DW) mixture including 5% wt CaCl_2 for 2, 5, 10 min to investigate the effect of coagulation time in the baths (Table 1). To analyze the effect of number of coagulation, the GO dispersion was immersed into coagulation bath with different concentrations of water and ethanol (Table 2). In Table 1, the number of coagulation bath as 5 means that GO dispersion is immersed to first then second, then third, then forth and finally fifth coagulation bath, as described in Table 2. The number of coagulation bath as 3 means that GO dispersion is immersed to first then second, then third coagulation bath as given in Table 2. In Table 1, the first number in the sample notation shows the number of coagulation bath, the second number with 'T' letter shows the coagulation time. For example; GO-1-T2 means that GO samples immersed just only first coagulation bath for 2 min (Table 2). To observe the effect of diamine molecules on GO fibres, 5 wt. % of ethylenediamine (DA_2) was added into the first coagulation bath containing 5 wt. % CaCl_2 .

Table 1 — Coagulation conditions in wet spinning process

Sample	Ingredients	Number of Coagulation baths	Coagulation time, min
GO- DA_2 - 5- T2	DA_2 + CaCl_2 /ethanol/DW	5	2
GO- 5- T2	CaCl_2 /ethanol/DW	5	2
GO- 3- T2	CaCl_2 /ethanol/DW	3	2
GO- 1- T2	CaCl_2 /ethanol/DW	1	2
GO- 3- T5	CaCl_2 /ethanol/DW	3	5
GO- 3- T10	CaCl_2 /ethanol/DW	3	10

GO—Graphene oxide fibre, DA_2 —Ethylenediamine, DW—Distilled water.

Table 2 — Ratio of ethanol and distilled water (DW) in coagulation bath

Coagulation bath	Ingredients
First	Ethanol (30% vol.) / DW (70% vol.) with % 5 wt CaCl_2
Second	Ethanol (40% vol.) / DW (60% vol.)
Third	Ethanol (50% vol.) / DW (50% vol.)
Fourth	Ethanol (60% vol.) / DW (60% vol.)
Fifth	Ethanol (80% vol.) / DW (80% vol.)

2.2.3 Characterization of Graphene Oxide Fibres

The morphological properties of the GO fibres were analyzed by scanning electron microscopy (SEM, Zeiss EVO MA10). Mechanical properties of the fibres were measured using a Usel, UNF15 tensile tester with 1 mm/min speed and 1 cm gauge length, according to the ASTM D3822-07 standard. Resistance measurements were carried out by using Microtest 6370 LCR two probe. Conductivities of the fibres were calculated by using the electrical resistance measured by the following equation:

$$K = \frac{L}{R \times A} \quad \dots (1)$$

where K is the coefficient of electrical conductivity (S/cm); R, the electrical resistance (Ω); A, the cross-sectional area (cm^2); and L, the fibre length (cm). Measurements were performed to 30 specimens for each sample to obtain an average value.

To analyze the functional groups, Fourier transform infrared spectroscopy (FT-IR) (Thermo, NICOLET, iS10) analysis was conducted to both GO dispersion without coagulation (GO reference) and sample GO- DA_2 -5-T2 and sample GO-5-T2.

The effect of ingredients of coagulation bath, the number of coagulation baths and coagulation time had been statistically analyzed. Variance analysis was performed by one way - ANOVA followed by Tukey Post-Hoc tests for the effect of the number of coagulation baths and coagulation time; whereas independent t test was conducted to define the effect of ingredients of coagulation bath. All statistical analysis was performed at a confidence interval of 95%.

3 Results and Discussion

Fibre coagulated by ethylenediamine (DA_2) at the first coagulation bath appears darker than fibre coagulated without DA_2 at the first coagulation bath. Thus, ethylenediamine is thought to affect the fibres as a reduction process, leading to darker shade, curly, rough and brittle structures, since partial reduction generally leads to an increase in rigidity, brittleness and color darkness¹⁷.

3.1 Effect of Coagulation Baths on Fibre Count

Tex values, showing the gram weight of 1000 m length of fibre are 22.50, 10.83, 11.36, 22.93, 12.00 and 11.43 tex for GO- DA_2 -5-T2, GO-5-T2, GO-3-T2, GO-1-T2, GO-3-T5, and GO-3-T10 respectively.

As can be seen, DA_2 addition results in the higher count. An increase in coagulation time does not cause

any clear differences in fibre counts i.e GO-3-T2, GO-3-T5, GO-3-T10 having 2 min, 5 min, 10 min respectively. On the other hand, the number of coagulation bath distinctly affects the fibre count (GO-5-T2, GO-3-T2, GO-1-T2). Increase in the number of coagulation bath improves coagulation; water drains off from GO dispersion to coagulation bath. Some dispersed graphene might leak to the coagulation bath during water draining off from GO dispersion to the coagulation bath. Thus, the increased number of coagulation may also increase the leakage of dispersed GO to coagulation bath together with an increase of water draining off from GO dispersion to the coagulation bath, up to a certain number of coagulation baths. This results in a decrease in the weight of fibre per unit length (reduction of tex amount). As a result, the minimum amount of GO leakage and water draining is expected to be in the one bath system, and the fibre count is highest at the one coagulation bath system. The maximum amount of water drainage and coagulation is observed in the three bath systems, so lowest fibre count and crinkly fibre are obtained in three coagulation bath systems.

To observe the functional groups in the structure, FT-IR spectroscopy has been performed to samples GO-DA₂-5-T2, GO-5-T2 and reference material (non-coagulated GO powder) (Fig. 1). The peaks observed in all 3 samples at 3344.04 cm⁻¹ wavelength correspond to -OH hydroxyl groups. The peak corresponding to C-N amine group due to ethylenediamine (DA₂) at 3500 cm⁻¹, which is suppressed under the peak of hydroxyl group results in the sharper peak at 3500 cm⁻¹. The peak for the reference GO powder at 1720.27 cm⁻¹ wavelength corresponding to C=O carbonyl groups disappears through coagulation bath. This might be due to the fact that carbonyl groups might be surrounded by

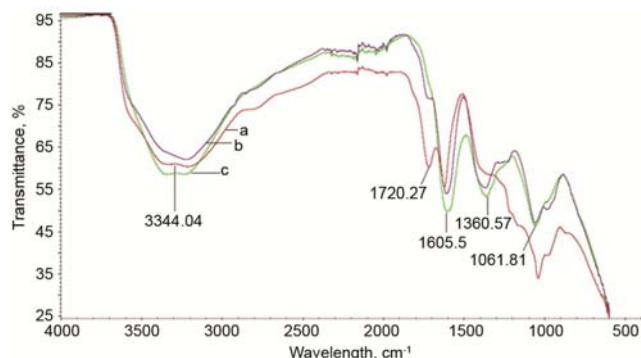


Fig. 1 — FT-IR spectroscopy of reference GO powder before coagulation (a), GO-5-T2 (b) and GO-DA₂-5-T2 (c)

Ca²⁺ ions and solvated by salts, or because of the formation of COO⁻ by ionization at the watery environment. The aromatic C=C peak caused by graphene at 1605.50 cm⁻¹ is observed in all three samples. However, the peak corresponding to NH₂ amine group due to ethylenediamine (DA₂) at 1600 cm⁻¹, which is suppressed under the peak of aromatic C=C peak results to sharper peak at 1600 cm⁻¹. Coagulated samples contain C-O carboxyl peak at 1360.57 cm⁻¹ wavelength. This peak is not observed in the reference GO sample, which might be a result of solvation with salts formed in the ethanol/water coagulation bath or ionization. All three samples contain the C-O alkoxy peak at 1060.81 cm⁻¹ wavelength (C-N) the amine group peaks, which are expected to be seen at 1100-1300 cm⁻¹, might be suppressed by C-O carboxyl peaks.

3.2 Morphological Properties of GO Fibres

The SEM images of GO fibres are shown in Fig. 2. As can be seen from the images, all the fibres are dense and aligned along the fibre axis. When the sample with ethylenediamine (GO-DA₂-5-T2) and sample without ethylenediamine (GO-5-T2) [Figs 2(a) and (b)] are compared, it can be said that sample with DA₂ has curlier and rough surface than that of the sample without DA₂ due to partial reduction effect of DA₂. When the effect of coagulation time on surface of fibre (2 min, 5 min and 10 min for sample GO-3-T2, GO-3-T5, GO-3-T10, respectively) [Figs 2 (c), (e) and (f)] is examined, it is obvious that an increase in coagulation time causes more even and smooth surface. This can be explained by the fact that the water drained from fibre into the coagulation bath during the first several minutes of coagulation is very evident, leading to crumple of GO flake and crinkly, rough fibre (as can be seen from sample GO-3-T2). However, as the time in coagulation bath progresses, the amount of ethanol transferred from the bath into the GO fibre increases leading to more even, smooth and plenary surface structure (as seen from GO-3-T5 and GO-3-T10).

As the number of coagulation bath increases (1 bath, 3 baths, 5 baths for sample GO-1-T2, GO-3-T2, GO-5-T2 respectively), roughness and crinkly structure of fibres increase. The sample produced with 1 bath (GO-1-T2) [Fig. 2(d)] does not completely coagulate because of less number of baths and higher water ratio in the bath. Thus, GO fibre taken from the first bath (GO-1-T2) contains a large amount of water in the structure leading to more swelled and smooth

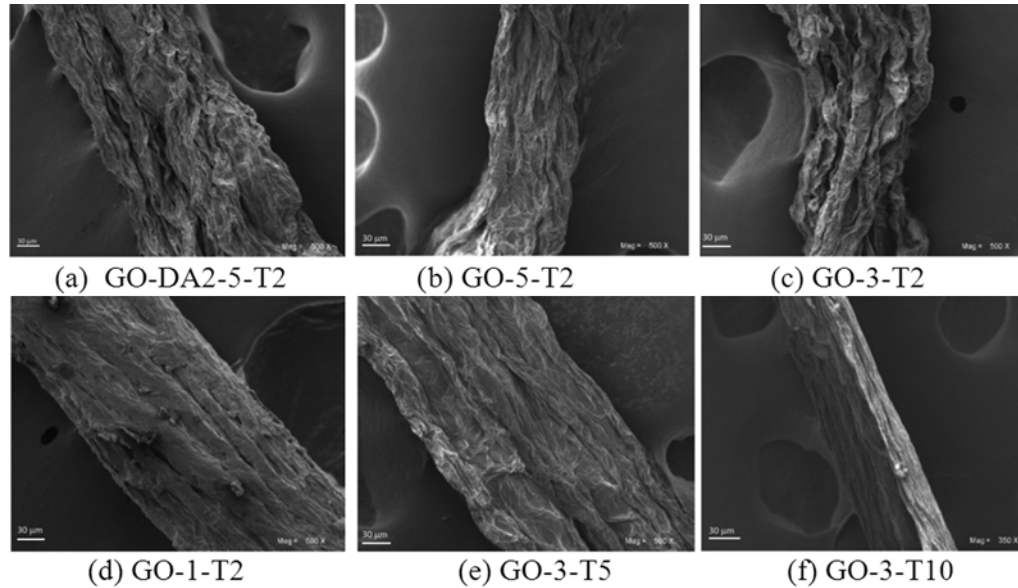


Fig. 2 — SEM images of GO fibres

surface and it requires a long drying time. It is observed that the sample with 3 baths has crinklier surface than the sample with 5 baths, because of more water drainage from GO dispersion into the coagulation bath (i.e. more coagulation). However, as the number of baths (more than 3 baths) increases, the amount of ethanol transferred from the bath into the GO fibre increases leading to more even, smooth surface structure.

3.3 Mechanical Properties of GO Fibres

The mechanical properties of GO fibres are shown in Table 3. During wet spinning process with ethylenediamine, the enhanced crimp and color darkness as observed, are indicators of partial reduction. With this reduction, some of the functional groups containing C-O-H move away, strong bonding between the layers is hindered, GO flakes become more rigid and the hydrogen bond and cross-linkages between rigid are reduced^{11,18}. Thus, the tenacity (strength) of the sample with DA₂ (GO- DA₂-5-T2) is less than the sample without DA₂ (GO-5-T2) and has lower strength among other samples. Breaking elongation is higher than that sample without DA₂ which might be due to crinklier structure [Figs 2(a) and (b)]. The effect of DA₂ on mechanical properties is found to be statistically significant according to independent t test performed.

If solvent (water) in the GO dispersion is drained very fast into coagulation bath or the fibre is not coagulated enough, i.e. solvent (water) in the GO dispersion is not drained enough into coagulation

Table 3 — Mechanical properties and electrical conductivity of GO fibres

Sample	Breaking strength cN/tex (CV%)	Elongation, % (CV%)	Electrical conductivity, S/cm (CV%)
GO- DA2-5-T2	0.234(28.197)	6.87(26.64)	2.39×10^{-04} (27.1)
GO-5-T2	3.471(14.465)	4.39(22.44)	7.76×10^{-04} (23.8)
GO-3-T2	3.726(30.203)	4.33(27.55)	3.25×10^{-04} (27.4)
GO-1-T2	0.179(26.828)	15.68(27.43)	1.77×10^{-02} (21.8)
GO-3-T5	2.730(24.202)	1.74(28.89)	3.56×10^{-03} (18.7)
GO-3-T10	2.073(27.058)	1.23(21.648)	3.87×10^{-03} (22.2)

bath, and water in the fibre structure evaporates in the course of the time, porosity in the fibre structure increases leading to decrease of fibre strength¹¹. Another fact is that, as the crinkly structure of the fibre increases, the strength improves because of an increase of pinch point. Thus, there is a tendency of decrease in tenacity and breaking elongation of fibre as the coagulation time increases for the sample GO-3-T2, GO-3-T5, and GO-3-T10.

Among samples with a different number of coagulation baths (1 bath, 3 baths and 5 baths for GO-1-T2, GO-3-T2, and GO-5-T2 respectively), the sample with 1 coagulation bath has less strength due to fast coagulation and late evaporation of heavy water rate during drying leading to the more porous structure. This sample has also the highest breaking elongation, which might be because of the contribution of porous, void structure into elongation during breaking. Contact with highly volatile solvents

such as ethanol causes shrinkage, crinkly and rigid structure on GO flakes and fibres¹¹. Thus, a decrease in breaking elongation of the sample with 3 or 5 baths compared to the sample with 1 bath may also result from an increase of ethanol ratio in bath and fibre structure. The mechanical properties of the samples are also compared statistically and the effect of the number of coagulation bath on mechanical properties is found to be statistically significant at the confidence interval of 95%. According to Tukey post hoc tests, the sample obtained with one coagulation bath (GO-1-T2) is found to be statistically different than the samples obtained from 3 and 5 coagulation baths (GO-3-T2 and GO-5-T2).

3.4 Electrical Conductivities of GO Fibres

Electrical conductivities of the fibres are shown in Table 3. As can be seen, the electrical conductivity of sample with DA₂ (GO- DA₂-5-T2) is similar to that of the sample without DA₂ (GO-5-T2). It is expected that partial reduction of fibre due to DA₂ results in an increase in the electrical conductivity; however, there is another mechanism that affects the electrical conductivity, i.e. contact point (contact area) of GO flakes (layers) within the fibre structure. It is expected that as the smoothness and planar contacts of GO flakes (layer) at the GO fibre increase, in other words as the crinkly structure of fibre decreases, the electrical conductivity network will increase, leading to an increase in electrical conductivity coefficients. Thus, although partial reduction increases electrical conductivity, the crinkly structure of sample with DA₂ causes a decrease in electrical conductivity.

Thus, samples spun from one coagulation bath with low crinkly structure and more planar graphene layers show highest electrical conductivity. Conversely, samples with high crinkly structure (3 or 5 coagulation baths) show low electrical conductivity. Another reason of low electrical conductivity of the sample with higher number of baths (3 and 5 baths) may also be the leakage of graphene oxide particles in GO dispersion into coagulation baths. The electrical conductivities of 5 and 3 bath samples are found to be statistically similar, whereas one bath sample has statistically significant difference compared to other samples with 5 and 3 baths. So, the increase in number of coagulation baths from 1 bath to 3 baths results in reduced electrical conductivity; however, further increase in the number of coagulation baths does not affect the conductivity significantly. The samples with

5 and 10 min coagulation times have higher electrical conductivity than the sample with 2 min coagulation bath, because of smoother and planar contacts of GO flakes (layers), all graphene oxide fibres manufactured are in the semiconductor range¹⁹.

4 Conclusion

4.1 Number of coagulation bath distinctly affects the fibre count, generally leading to a reduction in tex of fibre, while an increase in coagulation time does not cause any clear differences in fibre counts. The lowest fibre count and crinkly fibres are obtained in three coagulation bath systems.

4.2 An increase in coagulation time generally causes more even and smooth fibre surface. The tendency of an increase in roughness and crinkly structure has been observed as the number of coagulation bath increases from 1 bath to 3 or 5 baths. However, the sample with 3 baths has more crinkly surface than the sample with 5 baths, because of more water drainage from GO dispersion into the coagulation bath (i.e. more coagulation).

4.3 The samples spun from one coagulation bath have the highest electrical conductivity, while the sample with 3 or 5 coagulation baths has low electrical conductivity.

4.4 Among samples with a different number of coagulation baths, the sample with 1 coagulation bath has less strength with highest breaking elongation.

4.5 There is a tendency of decrease in tenacity and breaking elongation of fibre as the coagulation time increases.

4.6 Ethylenediamine results in lower strength and highest fibre count together with darker, curly and rough fibre structure.

All graphene oxide fibres manufactured are in the semiconductor range. Among the samples, the sample with 1 coagulation bath, 2 min coagulation time can be preferred if electrical conductivity property is more important than fibre tenacity property. However, if fibre tenacity property is more important than electrical conductivity property, the sample with 3 coagulation baths and 2 min coagulation time can be preferred.

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